BEITRÄGE ZUR KENNTNIS DER ALLOTROPEN MODIFIKATIONEN VON SCHWEFEL. III. UEBER DAS VERHALTEN VON JOD ZU SCHWEFEL UND SELEN.

Von C. R. PLATZMANN.

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Nach den bekannten Untersuchungen gibt es bisher keine Beweise für die Existenz von Jod-Schwefelverbindungen, zumal sich Jod kryoskopisch gegen Schwefel ebenfalls völlig indifferent verhält, wofür die nachstehenden Versuche—Schwefel in Jod und Jod in Schwefel gelöst—auch als Beweis angeführt werden mögen:

1. Kryoskopische Bestimmungen von präzipitiertem, löslichen Schwefel in Jod (Smp. 114°, K=204)[1]

Jod in gr.	Schwefel, Einzelmengen, gr.	Erniedrigung in grad.	Mol.-Gew.	Atome.
50	0.1338	0.214°	255	8.0
	0.1915	0.319	245	7.7
	0.1597	0.269	242	7.6

Auch plastischer, unlöslicher Schwefel lieferte unter Rückbildung identischer Lösungen, die gleichen Werte von normalem, S_8 entsprechendem Molekulargewicht.

2. Kryoskopische Bestimmungen von Jod in Schwefel (Smp. 114.5°, K=213)[2]

Schwefel in gr.	Jod, Einzelmengen, gr.	Erniedrigung in grad	Mol.-Gew.	Atome
25.0	0.2390	0.780	261	2.05
	0.2303	0.729	269	2.12
	0.2317	0.776	254	2.00
	0.2252	0.748	257	2.02

(1) E. Beckmann und R. Hauslian, *Z. anorg. allg. Chem.*, **80** (1913), 223.
(2) Vgl. die erste Abhandlung dieser Serie, dieser Bulletin, **4** (1929), 235.

Die experimentell ermittelte und offenbar für schmelzenden Schwefel allgemein gültige Konstante K=213 hat sich also auch in diesem Falle als brauchbar erwiesen und man kann demzufolge aus dieser Tatsache schliessen, dass durch Fremdmoleküle keine Veränderungen des Gleichgewichts beim Schmelzpunkt stattgefunden haben. Wenn trotzdem nach 24 Stunden in der erkalteten Schmelze, wenn diese Jod enthielt, mehr amorpher Schwefel gefunden wurde, als wenn diese jodfrei war, so wird man diese Erscheinung ebenso erklären können, wie das nachträgliche Verschwinden von amorphem Schwefel aus solchem, der mit NH_3 behandelt war und sekundäre Verschiebungen bei bezw. nach dem Erkalten annehmen dürfen.

Nach E. Beckmann besitzt Selen analog dem Schwefel in organischen Lösungsmitteln grosse Moleküle Se_8, die sich indessen in schmelzendem Jod bis zu Se_2 und Se_1 aufspalten, was angesichts der kleinen, 3–4 betragenden Dielektrizitätskonstante des Jods, nach welcher Jod nur geringen dissoziierenden Einfluss haben sollte, überraschend ist, um so mehr, als auch eine chemische Jod-Selen-Verbindung nicht hat nachgewiesen werden können.

Die Kryoskopie eröffnete hinsichtlich des Schwefels die Möglichkeit einer Nachprüfung des Verhaltens von Selen zu Jod und von Selen zu Schwefel.

Nach den Arbeiten von Bettendorf und vom Rath,[1] Muthmann[2] und Ringer[3] scheiden sich aus Selen-Schwefellösungen Mischkristalle aus monoklinem Schwefel und monoklinem Selen aus. Entsprechend wurden bei kryoskopischen Versuchen statt Erniedrigungen Erhöhungen des Gefrierpunkts beobachtet.

Bei der vermutlich vorhandenen Isomorphie ist anzunehmen, dass die Mischkristalle aus S_8 und dem analog zusammengesetzten Se_8 bestehen. Gleiche Molekulargrösse des Selens in der festen wie flüssigen Lösung setzt voraus, dass zwischen Gefrierpunkts- und Konzentrationsänderung eine feste Proportion besteht, für die in der Tat die folgenden Versuche als Bestätigung angesehen werden können, wenn man die schwere Löslichkeit des Selens und die verhältnismässig unsichere Einstellung des Gefrierpunktes berücksichtigt. Um das Selen schneller und leichter zu lösen, erwies es sich als vorteilhaft, Selen mit der vierfachen Menge Schwefel zusammenzuschmelzen und kurze Zeit bis zum Sieden zu erhitzen, worauf man die erkaltete Schmelze zu den Einzelbestimmungen benutzt, bei denen oft erst nach längerer Zeit Gefrierpunktskonstanz erreicht wird. Die kryoskopischen Versuche ergaben folgende Werte.

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(1) *Poggendorfs Annalen*, **139** (1870), 129.
(2) *Z. Kristallographie*, **17** (1890), 4.
(3) *Z. anorg. allg. Chem.*, **32** (1902), 183.

Vers. Nr.	Schwefel in gr.	Selen in %	Erhöhung nach Konstanz	Erhöhung auf 1% Se.
1	25.00	1.270	0.275	0.216
2	25.00	0.608	0.173	0.285
3	25.00	0.605	0.148	0.245
4	25.00	1.580	0.366*	0.230
5	25.00	1.283	0.303**	0.234

*Nach 2 Tagen. **Nach 1 Tag.

Obwohl die Konzentration bis zum Verhältnis 1:2.5 wechselt, bleibt die Enderhöhung ziemlich proportional und beträgt für 1% Selen im Mittel 0.242°. Das Molekulargewicht des Selens dürfte daher in der festen wie flüssigen Phase gleich gross sein und Se_8 in Analogie mit S_8, dem Molekül des isomorphen, monoklinen Schwefels.

Wenn die vorstehenden Annahmen richtig sind, so lässt sich mittels der in der ersten Abhandlung ermittelten kryoskopischen Konstante des Schwefels K=213 der relative Gehalt der festen Phase an Selen berechnen. Nach E. Beckmann und seinen Mitarbeitern[1] besteht bei ebullioskopischen Bestimmungen, wenn Substanz mit dem Lösungsmittel verdampft, folgende Beziehung:

$$\Delta = \frac{K \times \%}{m}(1-a) ,$$

wobei a das Konzentrationsverhältnis des gelösten Stoffes im Dampf einerseits, in der Flüssigkeit andererseits bedeutet. Diese Formel ist auch bei der Kryoskopie anwendbar, wenn gelöstes Material in die kristallinische Abscheidung des Lösungsmittels als feste Lösung mit übergeht. a bedeutet dann das Konzentrationsverhältnis des gelösten Stoffes in der Abscheidung einerseits in der Lösung andererseits. Im vorliegenden Falle sind

Δ berechnet auf 1% Se	−0.242°
m berechnet auf Se_8	633.6
K Mittelwert	213

Aus $\Delta = \frac{K \times \%}{m}(1-a)$ berechnet sich für:

$$1-a=-0.718$$

$$a=1.718$$

(1) *Z. physik. Chem.*, **17** (1895), 110; **58** (1907), 543; **86** (1914), 339.

In den Kristallen befindet sich also 1.7 mal mehr Selen als in der Lösung, aus der es abgeschieden ist.

Trägt man in eine geschmolzem Selen-Schwefelmischung Jod ein, ohne dass eine Aenderung der Selenmoleküle erfolgt, so muss bei der kryoskopischen Bestimmung die normale Molekulargrösse des Jods $J_2=254$ resultieren. Würden die Selenmoleküle indessen zu Se_2 oder Se_1 durch das Jod aufgespalten, so müsste sich eine grössere als vorauszusehende Gefrierpunktserniedrigung ergeben, ganz abgesehen von der in solchem Falle gänzliche ausfallenden Isomorphie und Mischkristallbildung. Entsprechende Versuche ergaben.

Konstantenbestimmung in Schmelzen von selenhaltigem Schwefel.

(a) Selengehalt, 1.58%; Erhöhung, 0.366° nach 2 Tagen.

Schwefel gr.	Gelöst gr. Einzelmengen	Erniedrigung	Badtemperatur beim		K Einzel best.
			Erstarren	Schmelzen	
1. Gelöst Jod, M (J_2)=254					
26.58	0.1361	0.362	114	116	179.6
	0.0984	0.318	113.7	115.6	218.2
	0.0947	0.304	113.7	115.2	216.7
2. Gelöst Diphenyl, M=154.1					
26.58	0.1355	0.675	112.6	115.2	204.0
	0.1125	0.555	112.6	114.5	202.1
	0.0842	0.408	111.6	114.0	198.5

(b) Selengehalt, 1.283%; Erhöhung, 0.303° nach 24 Stunden.

Schwefel gr.	Gelöst gr. Einzelmengen	Erniedrigung	Badtemperatur beim		K Einzel best.
			Erstarren	Schmelzen	
1. Gelöst Jod, M (J_2)=254					
26.28	0.0890	0.278	113.	116.0	208.5
	0.1013	0.346	113.3	115.7	228.0
	0.1139	0.371	113.0	115.3	217.4
2. Gelöst Diphenyl, M=154.1					
26.28	0.1144	0.611	112.4	115.0	216
	0.1358	0.694	111.7	114.4	207

Da die Konstanten nach den vorstehenden Versuchen sowohl bei Gegenwart von Selen mit Jod wie auch die mit Diphenyl zur Kontrolle erhaltenen um $K=213$ liegen, deutet nichts auf eine Verschiebung des Gleichgewichts bezw. Aufspaltung des Selens durch Jod.

Zur weiteren Prüfung dienten umgekehrt die verwendeten Jod-Selen-Mischungen zur Bestimmung der Konstanten in Schwefel.

Melokulargewicht von Jod-Selen-Schmelzen beim Eintragen in geschmolzenen Schwefel.

Annahmen:—1. 1.283% Se=0.303° Erhöhung,
2. Schwefel $K=213$,
3. Jod, Mol. Gew.=254.

(a) Verwendete Schmelze von 74.23 Jod und 25.77 Selen.

Vers. Serie	Schwefel gr.	Schmelze, gr. Einzelmengen	Gefundene Erniedrigung	Mittleres Mol. der Schmelze
A_1	25.00	0.2501	0.580	367
		0.2512	0.614	347
		0.2546	0.627	347
		0.2495	0.577	369
A_2	25.00	0.2482	0.590	358
		0.2497	0.616	345
		0.2509	0.598	356

Kontrolle der Konstanten mit Diphenyl.

Schwefel gr.	Gelöst, gr. Einzelmengen	Erniedrigung	K
25.00	0.1378	0.789	221
	0.1338	0.679	196

(b) Verwendete Schmelze von 60.17 Jod und 39.83 Selen.

Vers. Serie	Schwefel gr.	Schmelze, gr. Einzelmengen	Gefundene Erniedrigung	Mittleres Mol. der Schmelze
B_1	25.00	0.2553	0.404	537
		0.2520	0.429	501
		0.2509	0.427	499

Kontrolle der Konstanten mit Diphenyl.

Schwefel gr.	Gelöst Einzelmengen	Erniedrigung	K
25.00	0.1427	0.806	218
	0.1024	0.510	192

Vers. Serie	Schwefel gr.	Schmelze Einzelmengen	Gefundene Erniedrigung	Mittleres Mol. der Schmelze
B_2	25.00	0.2546	0.405	536
		0.2496	0.470	452
		0.2509	0.496	429

Kontrolle der Konstanten mit Diphenyl.

Schwefel gr.	Gelöst Einzelmengen	Erniedrigung	K
25.00	0.1408	0.781	213.7
	0.1267	0.651	197.9

Es ergibt sich demnach, dass das Schmelzpunktsgleichgewicht des Schwefels durch den Gehalt an Selen und Jod nicht verändert wird, da die Kontrollen mittels Diphenyl allgemein normale Schwefelkonstanten lieferten. Die eingetragenen Selen-Jodmischungen lieferten höhere Molekulargewichte und es wurden mit der an Selen reicheren Mischung die relativ höchsten Molekularwerte erhalten, wie es auch der Annahme von Se_8=633.6 entspricht.

Der erste Wert jeder Serie möge deswegen etwas genauer untersucht werden, weil durch das Vorerhitzen über Nacht die hierbei erzielte Einstellung des Gleichgewichts besonders präzis erscheinen muss. Wäre das Selen in der jodhaltigen Schwefellösung wie in seiner Lösung in blossem Schwefel als monoklines Se_8 vorhanden, so müsste die gefundene kryoskopische Erniedrigung sich aus der dem Selengehalt (Se_8=633.6) entsprechenden Erhöhung

$$\Delta_1 = \frac{213 \times \%Se_8}{633.6}(-0.718) \quad \text{oder} \quad -\frac{213 \times \%Se_8 \times 0.718}{633.6}$$

und der dem Jodgehalt entsprechenden Erniedrigung

$$\Delta_2 = \frac{213 \times \%J_2}{254}$$

additiv als $\Delta_1 + \Delta_2 = \Delta$ berechnen lassen. Die entsprechende Rechnung ergibt für die ersten Werte der Serien A_1, A_2, B_1 und B_2.

Vergleich der gefundenen Erniedrigung mit der berechneten.

Versuch	Gefundene Erniedrigung	Berechnete Erniedrigung
A_1	−0.580°	−0.622+0.061=−0.561
A_2	−0.590°	−0.618+0.060=−0.558
B_1	−0.404°	−0.515+0.097=−0.418
B_2	−0.405°	−0.515+0.096=−0.419

Mit Rücksicht auf die labilen Gleichgewichtsverhältnisse ist die Übereinstimmung im Rahmen der unvermeidlichen Fehlergrenzen als ausgezeichnet anzusehen.

Man muss also nunmehr als richtig unterstellen, dass Selen, welches in schmelzendem Jod zu Se_1 und Se_2 aufspaltet, durch Auflösen der Jodselenschmelze in Schwefel grosse Moleküle Se_8 zurückbildet, was um so interessanter ist als Jod und Schwefel hinsichtlich Schmelztemperatur und Dielektrizitätskonstante, wie folgt übereinstimmen.

	Schmelztemperatur	Dielektrizitätskonstante
Jod	114°	4.0
Schwefel	114.5°	3–4

Es müssen also noch andere Einflüsse spezifischer Art in diesem Falle die Verschiedenheit von Jod bezw. Schwefel gegenüber bedingen. Dass es sich um einfache, leicht verschiebbere Dissoziation handelt, zeigt nicht nur die Veränderlichkeit des Moleküls mit der Natur des Lösungsmittels, sondern auch mit der Konzentration. Nachdem Olivari[1] in Jodlösung Moleküle Se_2 festgestellt hatte, konnten E. Beckmann und R. Hanslian[2] nachweisen, dass bei grösserer Verdünnung in Jodlösung die Aufspaltung bis Se_1 geht, woran Temperaturerhöhungen bis 183° (Siedepunkt des Jods) nichts änderten.

(1) *Rend. Acc. Lincei*, [5] **17** II (1908), 391.
(2) *Z. anorg. allg. Chem.*, **80** (1913), 224.

Kryoskopisch		Ebullioskopisch	
Konzentration	Molekül	Konzentration	Molekül
0.22–2.05%	$Se_{1.33-1.78}$	0.165–2.80%	$Se_{1.36-1.88}$

Nach Olivari liefert Selen sowohl in Quecksilberchlorid (Schmelzpunkt 277°)[1] wie in Quecksilberbromid (Schmelzpunkt 253°)[2] mit steigender Konzentration assoziierende Moleküle. Auch diese Beobachtung spricht dafür, dass es sich in Selen-Jod-Lösungen um einfache Dissoziationen unter dem spezifischen Einfluss des Lösungsmittel handelt. Das Schwefelmolekül S_8 ist hingegen auch bei diesen Lösungsmitteln und Temperaturen beständig. Immer wieder zeigt sich, dass der Einfluss des Lösungsmittels denjenigen der Temperatur erheblich übertreffen kann.

Zusammenfassung.

1. Selen liefert in Schwefel gelöst kryoskopische Erhöhungen infolge der Bildung von Mischkristallen aus Selen und Schwefel. Nach den mitgeteilten Versuchen sind diese aus isomorphen Mischungen von monoklinem Schwefel (S_8) und monoklinem Selen (Se_8) zusammengesetzt.

2. Selenhaltige Schwefellösungen geben sowohl mit Diphenyl wie mit Jod normale Konstanten so, dass also durch Selen die Gefrierpunktsverhältnisse nicht geändert werden, was als ein Beweis dafür zu werten ist, dass Selen und Jod eine Verbindung eingehen oder aber in der Schwefellösung eine Aufspaltung des Selenmoleküls herbeigeführt wird.

3. Das beobachtete kleine Selenmolekulargewicht (Se_2—Se_1) in Jodlösungen ohne Gegenwart von Schwefel, das grosse (Se_8) bei dessen Anwesenheit als Lösungsmittel erscheint um so interessanter, als Schmelztemperatur und Dielektrizitätskonstante bei Jod und Schwefel fast vollkommen übereinstimmen und nur geringe Dissoziation erwarten lassen.

Hamburg, Deutschland.

(1) *Rend. Acc. Lincei*, [5] **18** II (1909), 94.
(2) *Rend. Acc. Lincei*, [5] **21** I (1912), 718.

BIOCHEMICAL STUDIES ON RICE STARCH. III. THE ACTION OF ENZYMES ON RICE STARCH. I.

By Wei Sun TAO.

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The experimental results of researches into the complex metabolic processes which take place in the reserved starch during the germination of the seeds have been described briefly in the previous article, and the transformation of the starch molecule into simpler sugars was assumed to take place successively by the action of the hydrolytic enzymes such as amylase or diastase which, according to the opinion of Brown and Morris, seems to occur in the seedlings by a direct glandular secretion of the columnar epithelium of the embryo.

The idea that the conversion of starch into sugars by the action of the diastase formed and diffused slowly out of the epithelium during germination, was confirmed by the experiment upon rye by Haberlandt.(1) The process of germination thus shows that as it commences, active metabolism, synchronous with the dissolution of the cell-walls and the transformation of starch, goes on in the epithelium.

There are two kinds of vegetable diastase, one of which named translocation diastase acts on starch grains to convert them slowly into sugar, the optimum temperature being said to be 45–50°C., and the other one is "diastase of secretion," which corrodes starch grains and disintegrates them before dissolution, and the working temperature is around 50–55°C., and the latter enzyme plays an important part for the conversion of starch into sugars during the germination.

As a matter of fact, the diastase from germinated barley was found to be capable of corroding and dissolving the starch of barley, wheat, rice and maize but to have no evident action on that of the potato, and the kidney-bean.

The optimal temperature for the diastase in germinated grains is said to be 54–56°,(2) and the activity of the enzymes is usualy increased or retarded by the presence of various salts.(3)

The optimum temperature for the germination of the rice grain is said to be 30° to 35°, and actually the transformation velocity of the starch in

(1) *Ber. Deut. botan. Ges.*, **8** (1890), 40.
(2) J. Effront, *Compt. rend.*, **174** (1922), 18.
(3) C. Oppenheimer, "Die Fermente u. Ihre Wirkungen," (1924–6); H. C. Sherman and A. W. Thomas, *J. Am. Chem. Soc.*, **37** (1915), 623.

the plant tissues is noticed to be greatest at 35°, where the diastase occurs in the embryo, and this fact seems apparently to contradict the experimental results in vitro that the optimal temperature of diastase extracted from germinated grains is situated at 54–56°, and the discrepancy between the two cases will be attributed to the presence of some accelerating agents for the action of the enzymes in vivo.

The action of the diastases prepared from malted barley and rice on the starch solution in vitro was investigated.

In the experiments, diastatic enzymes were prepared by extraction with 100 c.c. of distilled water at room temperature for 3 hours from 5 grams of the malted barley and germinated rice which were previously powdered, the insoluble residue being filtered off, and the brown coloured filtrate was used.

The substrate which was used in studying the action of the enzymes, was prepared with many precautions, as the impurities associated with starch, such as protein, exert some influence on the diastatic action of enzymes.[1]

The various starch solutions were prepared as follows:

(1) The rice starch was prepared from ground rice-powder after treating with petroleum ether, and a 0.3% NaOH solution to remove the fat and the protein. The 1% solution of this starch was used, the reducing power of the solution is zero.

(2) Soluble starch was prepared by Lintner's method. Digest the starch with 7.5% HCl for 7 days at room temperature, wash with water till the washing shows a neutral reaction to litmus, filter and dry. The reducing power of this solution is 1.5.

(3) Amylose and amylopectin were prepared by the method proposed by Gatin and Gruzewska, from the rice starch by means of a 1% NaOH solution. The reducing power of amylose and amylopectin is 3.1 and zero respectively.

To 20 c.c. of the 1% starch solutions, 4 c.c. of the extracts were added, and the mixture was left to stand for 15 minutes at 20°C., 30°C., 40°C. and 50°C. respectively. After a certain time of reaction, the reducing power of each solution was determined on one hand, and on the other the colour test for the iodine solution was studied.

In the following tables, the reducing power of the starch solution examined was shown by subtracting the value original to the extracts from that of the whole of the reaction system. The conversion of the starch solutions into simpler sugars by the enzymes was carried out with progressive velocity at a higher temperature.

(1) S. A. Waksman and W. C. Davison, "Enzymes," (1926), p. 154.

Rice Diastase.

	Rice starch		Soluble starch		Amylose		Amylopectin	
	I.	R.P.	I.	R.P.	I.	R.P.	I.	R.P.
Without enzymes	Blue	0	Blue	1.5	Blue	3.1	Blue	0
With enzymes 20°C.	blue	3.1	violet blue	5.5	purple	4.7	blue	3.9
With enzymes 30°	violet blue	7.8	violet blue	9.5	purple	7.8	blue black	6.9
With enzymes 40°	violet blue	9.5	red violet	16.4	red violet	16.4	blue	12.4
With enzymes 50°	violet blue	17.3	red violet	25.0	red violet	21.0	blue	18.9

Barley Diastase.

	Rice starch		Soluble starch		Amylose		Amylopectin	
	I.	R.P.	I.	R.P.	I.	R.P.	I.	R.P.
Without enzymes	Blue	0.	Blue	1.5	Blue	3.1	Blue	0
With enzymes 20°C.	violet blue	42.9	violet blue	51.5	violet	39.9	blue	35.8
With enzymes 30°	,,	46.1	,,	55.5	red violet	44.6	violet blue	42.7
With enzymes 40°	,,	49.2	,,	59.3	light violet	45.2	,,	46.9
With enzymes 50°	violet	52.6	violet	84.2	yellow	50.1	light violet	56.8

The malted rice acts on soluble starch more easily than on the other starch solutions, and this fact would be ascribed to the occurrence of a subtance promoting the enzyme activity in the soluble starch. The case is also noticed in the action of the malted barley extract on the starch solutions. However, there was noticed a marked difference between the two malt extracts in their hydrolytic action on the starch solution, especially in the temperature effect; the activity of the malted rice extract was increased markedly by increase of temperature, while the malted barley extract remains almost constant in its activity throughout the different temperatures. The optimal temperature for the action of these extracts in vitro seems to lie at about 50°, as is described in the literatures.

In the next experiment, both the rice amylase and the barley amylase were prepared in a purified state by the method of Sherman from both extracts, which show no reducing power, and acted on the starch solutions.

2.3 mg. of the barley diastase and 2.9 mg. of the rice diastase acted on the 1% solutions of 50 mg. of the starches for 15 minutes at 24°C., the reducing power of the solution, and the colour reaction for the iodine solution, were studied.

Rice Diastase.

Substrate	Rice starch solution		Soluble rice starch solution	
	Iodine-colour	R.P.	Iodine-colour	R.P.
	light violet	50.0	light violet	51.6

Barley Diastase.

Substrate	Rice starch solution		Soluble rice starch solution	
	Iodine-colour	R.P.	Iodine-colour	R.P.
	violet	57.8	violet	63.1

As will be seen from the above results, the hydrolytic action of the barley diastase on both the rice starch and the soluble starch shows no marked difference between them, and also the diastases prepared fairly in a pure state from both seeds show a similarity in the hydrolytic action on rice starch at 24°C., though they behave in their malt extracts with a different activity toward the same substrates.

In conclusion, the writer states that the diastases from different kinds of germinated grains behave in a different manner in their activity toward the same starch, and that the activity of the enzyme depends upon its purity.

July, 1928. Laboratory of Organic- and Bio-Chemistry,
Kyoto Imperial University.

BIOCHEMICAL STUDIES ON RICE STARCH. IV. THE ACTION OF ENZYMES ON RICE STARCH. II.

By Wei Sun TAO.

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In the first communication on this subject, the writer stated that the substances transformed from the reserve starch by germination were different, due to the influence of temperature on the reaction; when the seeds germinated at a low temperature, the simple sugars formed were composed mostly of sucrose with some maltose, and the formation of maltose is favorable at a high temperature. In the chemical reactions in vitro, the temperature is regarded as only changing the reaction velocity. Chemical reactions of combination and intramolecular transformation, in general, only take place within certain limits of temperature, and cannot be accomplished outside those limits. However, we can hardly believe that sucrose will form from starch at 20°, while maltose at a higher temperature.

The writer, therefore, took up the study of the reaction products from rice starch in vitro by the action of the rice diastase prepared from the germinated rice at 20°C. and 35°C. in order to learn what the chemical changes that occur in the plant tissues at different temperatures.

The rice diastase used in the present experiment was prepared from the rice seedlings by the method proposed by Sherman and Schlesinger and acted on the rice starch, both the rice diastase and the rice starch were obtained from the grains produced in the same rice field, 1928, which were used in the previous experiments.

In the experiment, the rice diastase acted on 15 gr. of the rice starch in 3% solution for 3 hours at 20° and 35°C. respectively. The reaction products were treated with 80%, 90% and absolute alcohols to separate by fractional precipitation as in the case of the rice seedlings, and the separated products were examined as to their rotatory power and reducing power in their aqueous solutions, and also the reaction for the iodine solution, and also for the Pinoff reagent, and the results are summarized in the following table:

Reaction Products at 20°C.

Fraction	Yield	$[\alpha]_D$	R.P.	Iodine test	Pinoff's test
80% alcohol ppt.	2.6 gr.	160	7	wine red	—
90% alcohol ppt.	1.0	137	23	brown	—
abs. alcohol ppt.	0.1	83	46	nil	—
Sum	3.7				

Reaction Products at 35°C.

Fraction	Yield	$[\alpha]_D$	R.P.	Iodine test	Pinoff's test
80% alcohol ppt.	3.6 gr.	179	74	wine red	—
90% alcohol ppt.	2.3	117	26	brown	—
abs. alcohol ppt.	1.2	95	43	nil	—
Sum	7.1				

In vitro, 50% of the starch by the rice diastase at 35° were converted into simpler sugars, and at 20°C. only 33% were transformed, while in the germinated seeds, 20% and 17%, of starch were converted into simpler substances; at the corresponding temperatures. From the comparison of these figures we have learned that the transformation of starch will be performed in a parallel way both in vitro and in vivo, and also that the disappearance of the sugar molecule by decomposing into carbon dioxide and water will happen in vivo while in vitro it is never met with.

The 80% alcohol precipitate in both cases as in vitro, which shows a wine red colour to iodine, and is judged to be composed mostly of dextrins from the data of the rotatory power and the reducing power, and these results agree quite well with these in the corresponding state in vivo.

The 90% alcohol precipitate was assumed also from its physical and chemical properties to be composed mostly of maltose with some glucose while the absolute alcohol precipitate was predominant in glucose in two cases, and both of the precipitates was lacking in sucrose as indicated in the Pinoff test.

The fact that the formation of reducing sugars is favorable at high temperature, was already noticed by the writer in the germination of seeds.

To the writer's interest, the formation of cane sugar was actually noticed in vivo, but not in vitro. We noticed further a great difference between in vivo and in vitro, in the chemical reactions which take place in the starch molecule, the decomposition of starch into carbon dioxide and water, the so-called respiration, prevailed in the case of in vivo.

In closing, the writer would like to offer her hearty thanks to Prof. Komatsu of Kyoto Imperial University, for these experiments were performed under his kind direction and neverfailing encouragement.

October 1929. Laboratory of Organic- and Bio-Chemistry,
Kyoto Imperial University.

SINOMENINE AND DISINOMENINE. PART XV. ON THE REDUCTION OF BROMO-SINOMENINE WITH NASCENT HYDROGEN.

By Kakuji GOTO and Reikichi INABA.

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In the XI communication,[1] one of the authors (K. G.) studied, in cooperation with H. Sudzuki, the reduction of sinomenine with nascent hydrogen and determined the following four facts.

1. Two molecules of sinomenine can be linked together with Na-amalgam reduction and give bis-8,8′-demethoxy-dihydrosinomenine.

2. Dihydrosinomenine gives by Na-amalgam reduction demethoxy-dihydrosinomenine, i.e., *d*-form of dihydrothebainone.

3. Sinomenine gives by Clemmensen's Zn-amalgam reduction in the hot demethoxy-desoxo-dihydrosinomenine, i. e., *d*-form of β-tetrahydro-desoxy-codeine.

4. The double linking of sinomenine can be reduced with nascent hydrogen, such as zinc and hydrochloric acid or Zn-amalgam and hydrochloric acid in the cold. The dihydrosinomenine thus obtained is identical with that produced by catalytic hydrogenation of sinomenine.

The research communicated in this report was carried out with the view to determine whether the bromo-sinomenine behaved in the same way as with sinomenine against these reducing agents. The results were completely affirmative as are shown in the following diagrams.

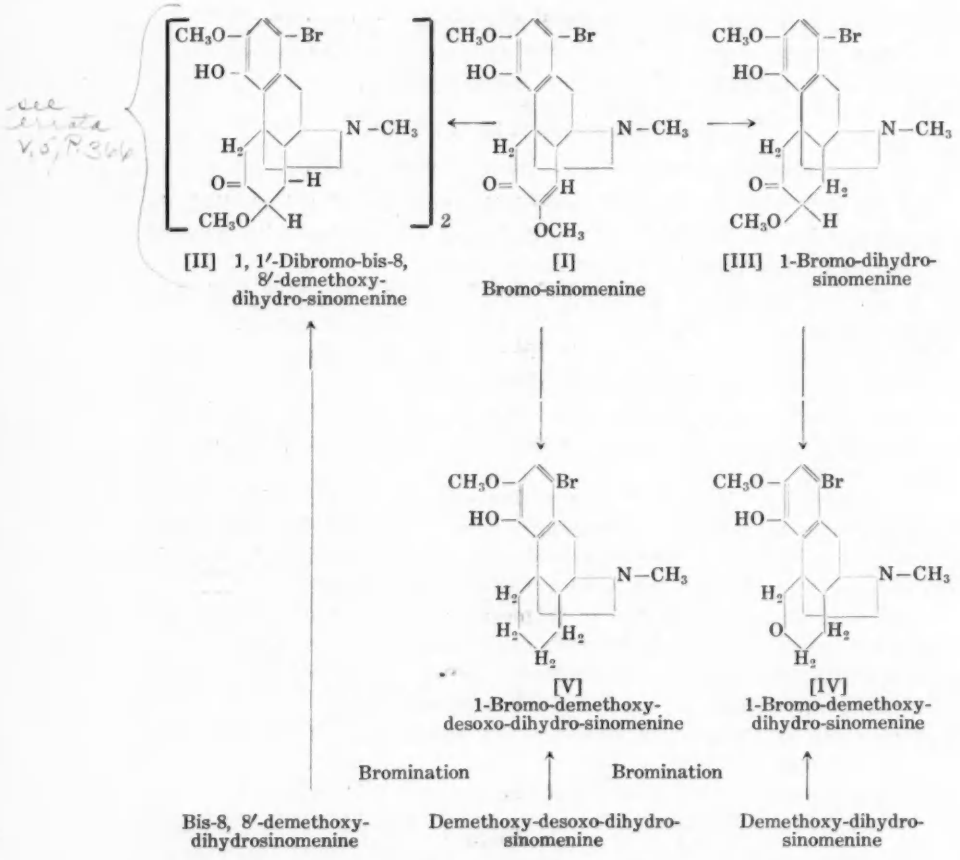
Properties of these substances may be summarised in the following table for convenience's sake.

Table 1.

	1. 1′-Dibromo-bis-8,8′-demethoxy-dihydro-sinomenine	1-Bromo-demethoxy-dihydro-sinomenine	1-Bromo-demethoxy-desoxo-dihydro-sinomenine	Brominated β-tetrahydro-desoxycodeine
Yield	20%	40%	30%	50%
Crystal form	granular	prisms	prisms	prisms
M.p.	227°	119°	127°	127°
$[\alpha]_D$	+19.02°	+57.57°	+40.44°	-39.52°
M.p. of oxime	237° (dec.)	263°	—	—
M.p. of iodomethylate	253–255°	119° (sinters) 127° (dec.)	253–255°	—
$FeCl_3$-react. in alcohol	green	green	green	green
Diazo-reaction	400,000*	200,000	50,000	10,000
$FeK_3(CN)_6$-reaction	no	+only in 1,000th	no	no
Formaline-SO_4H_2	greenish blue	greenish blue	yellowish brown	yellowish brown

* The figures show the dilution, at which the colour is still visible.

(1) This Bulletin, **4** (1929), 244.



By the reduction with Na-amalgam, bromo-sinomenine gave a substance of a bimolecular weight $(C_{18}H_{21}BrNO_3)_2$ in a yield about 20–40%, which melted at 227° and showed the properties given in the first column of the Table 1. Since the identical substance could be prepared by the bromination of bis-8,8′-demethoxy-dihydrosinomenine, it is clear that by the Na-amalgam reduction bromosinomenine is also linked together on its double linking. And from the same reasoning as was applied to the bis-8,8′-demethoxy-dihydro-sinomenine, it can be assumed that the linking point must be C_8 of each bromo-sinomenine molecule.

Secondly, bromo-dihydrosinomenine gave by the reduction with Na-amalgam, a substance $C_{18}H_{22}BrNO_3$ whose melting point was at 119°. Since

the identical substance was also obtained by the direct bromination of demethoxy-dihydro-sinomenine, it is clear that the substance is nothing but brom-demethoxy-dihydro-sinomenine. Thus the action of Na-amalgam on bromo-dihydro-sinomenine is also the splitting off the methoxyl group, vicinal to the ketone, as was with dihydro-sinomenine.

Thirdly, by the Clemmensen's reduction of bromo-sinomenine, bromo-demethoxy-desoxo-sinomenine was obtained in 30% yield. The substance was checked by the bromination of demethoxy-desoxo-sinomenine, which gave the identical substance. The action of the zinc-amalgan and hydrochloric acid in the hot is, thus, the reduction of the double linking, the elimination of the methoxyl group and the reduction of the ketone to the methylene group. It is rather interesting to note that such complicated reactions could be effected in such a short lapse of time with tolerably good yield.

Moreover, the bromo-demethoxy-desoxo-dihydro-sinomenine ($[\alpha]_D = +40.44$) was racemised effectively with brominated β-tetrahydro-desoxy-codeine ($[\alpha]_D = -39.52$) prepared from codeine. This brings forward another evidence that the demethoxy-desoxo-dihydrosinomenine is the optical antipode of β-tetrahydro-desoxy-codeine. Hence, at least the three asymmetric carbon atoms C_{13}, C_{14} and C_9 of sinomenine must be arranged so as to form the image of the corresponding asymmetric carbon atoms of the reduced derivatives of codeine and thebaine.[1]

Fourthly and lastly, bromo-sinomenine was reduced with granular zinc and hydrochloric acid in the cold. Yield of bromo-dihydro-sinomenine was here about 30%.

Experimental.

1,1′-Dibromo-bis-8,8′-demethoxy-dihydro-sinomenine [II]. (1) Bromo-sinomenine (5 gr.) was reduced in 2% caustic soda solution (50 c.c.) with 5% Na-amalgam (30 gr.). After 72 hours, the aqueous part, diluted with water (150 c.c.), was saturated with carbonic acid gas. The precipitate was dissolved in chloroform. The residue of the evaporated chloroform crystallised out on addition of acetone. The yield of the raw material was 1.2 gr., viz. 34.3% of the theoretical. It was redissolved in dilute caustic soda, precipitated with CO_2 and again recrystallised from acetone. The substance has a nice appearance of crystals, but, on examination with microscope, it consisted from granules, showing no angles. It melted at 227° and darkened at 274°.

(1) Loc cit., p. 252.

(2) Bromination of bis-8,8′-demethoxy-dihydro-sinomenine (2 gr.) with bromine (1 gr.) in glacial acetic acid solution in the way already given, resulted in the same substance as above. The yield amounted to 70%. The melting point was at 227°, which was unaltered with the admixture of the substance obtained in the reaction (1).

As regards other properties of this substance, see the first column of the Table 1.

Anal. Found: C=56.77; H=5.56; N=3.42; Br=20.49, 20.61%. Calc. for $(C_{18}H_{23}BrNO_3)_2$=758: C=56.98; H=5.58; N=3.69; Br=21.08%.

Mol. wt. Found (in glacial acetic acid): 807. Calc.: 758.

Sp. rotatory power: 0.3549 gr. subst. was dissolved into 25 c.c. alcoholic solution. l=1 dm.; α=+0.27; $[\alpha]_D^{13}$=+19.02.°

Oxim: M.p. 237 (dec.) Found: N=7.09%. Calc. for $(C_{18}H_{24}BrNO_4)_2$: N=7.10%.

Iodomethylate: M.p. 253～255°. Yield 80%. Crystallises in stout prisms, when aqueous solution is very slowly cooled. Found: J=24.33%. Calc.: I=24.36%.

1-Bromo-demethoxy-dihydro-sinomenine [IV]. (1) Bromo-dihydro-sinomenine (5 gr.) was reduced in 2% caustic soda solution (60 c.c.) with 5% Na-amalgam. (36 gr. divided in two portions). After five days, when the alkaloid was completely dissolved, the aqueous part was treated as was given with 1.1′-dibromo-bis-8,8-demethoxy-dihydro-sinomenine. The reduced substance can be recrystallised from a small quantity of acetone. M.p. 119°. Yield 1.2 gr., viz. 35% of the theoretical.

(2) Bromination of demethoxy-dihydro-sinomenine, in the same way as was given above, resulted in the same 1-bromo-demethoxy-dihodro-sinomenine, which melted at 119°. The admixture of this substance with that obtained by the above reduction (1) did not lower the melting point. The yield was almost quantitative.

The properties of 1-bromo-demethoxy-dihydro-sinomenine are given in the second column of the Table 1.

Anal. Found: C=56.70; H=5.77; N=3.30; Br=20.97%. Calc. for $C_{18}H_{22}BrNO_3$: C=56.83; H=5.83; N=3.68; Br=21.02%.

Sp. rotatory power: 0.2866 gr. subst. was dissolved into 10 c.c. alcoholic solution. l=1 dm.; α=+1.65. $[\alpha]_D^{13}$=+57.57°.

Oxime: prepared in the ordinary way. Prisms, when precipitated with sodium carbonate from water. M.p. 263° (dec.) Found: N=6.98%. Calc.: N=7.08%

Iodomethylate: can be recrystallised from water very slowly. Fine prisms collected in globules, which sinter at 119° and decompose at 127°. Found: I=24.57%. Calc.: I=24.31%.

1-Bromo-demethoxy-desoxo-dihydro-sinomenine [V]. (1) Bromo-sinomenine hydrobromide (ca. 10 gr.) was added to Clemmensen's Zinc amalgam (a large quantity) and the mixture was first poured on with 20 c.c. hydro-

chloric acid (1:1). While the reaction mixture was heated in the boiling water bath for one and half hours, the fuming hydrochloric acid was added from time to time (30 c.c. in three portions).

The isolation took place as was given in the XI communication.[1] The bromo-demethoxy-desoxo-dihydro-sinomenine, thus obtained, can be recrystallised from acetone in prisms. M.p. 127°. Yield 2.2 gr. i.e. 30% of the theory.

(2) Bromination of demethoxy-desoxo-dihydro-sinomenine, in the way frequently cited, gave the above substance in 80% yield.

The mixed melting point of these two substances, prepared in the different way, remained unaltered (127°).

As regards the properties of this substance, see the third column of the Table 1.

Anal. Found: C=59.42; H=6.70; N=3.78; Br=21.08%. Calc. for $C_{18}H_{24}BrNO_2$: C=59.01; H=6.55; N=3.82; Br=21.83%.

Sp. rotatory power: 0.3066 gr. subst. was dissolved into 10 c.c. alcoholic solution. l=5 cm.; α=+0.62. $[\alpha]_D^{12}$=+40.44.°

Racemisation of Bromo-demethoxy-desoxo-dihydro-sinomenine with Brominated β-Tetrahydro-desoxy-codeine. β-Tetrahydro-desoxy-codeine (0.5 gr.; m.p. 149°) was brominated in acetic acid (5 c.c.) with bromine (0.25 gr. in 5 c.c. acetic acid). The brominated substance melted at 127° and showed the properties given in the fourth column of the Table 1. Yield good. (Found: Br=21.94%. Calc. for $C_{18}H_{24}BrNO_2$: Br=21.83%).

Sp. rotatory power: 0.2935 gr. was dissolved into 10 c.c. alcoholic solution. l=5 cm.; α=−0.58. $[\alpha]_D^{13}$=−39.52.°

Racemisation. The substances used in the above two estimations of the rotatory power were mixed together and, after evaporation of alcohol, recrystallised from a little acetone. Ca. 0.33 gr. of the substance was collected in this way. It sintered at 119° and decomposed at 122°. When 0.3213 gr. of this substance was dissolved into 10 c.c. alcoholic solution and examined on its rotatory power in the tube of 1 dm., it did not rotate the polarised light.

Reduction of Bromo-sinomenine with Zinc and Hydrochloric Acid [III]. Bromo-sinomenine (1 gr.) was suspended in 4% hydrochloric acid (30 c.c.) and reduced with granular zinc (5 gr.). At the interval of one hour, 10% HCl (10 c.c. each) was added five times. After 24 hours, the aqueous part was filtered and the reduced base was isolated in the ordinary way. As bromo-dihydro-sinomenine is very difficultly soluble in boiling

(1) This Bulletin, 4 (1929), 252.

ethyl alcohol, it could be purified easily. M.p. 236°. Admixture with bromo-hydro-sinomenine (m.p. 237°) prepared by the bromination of dihydro-sinomenine did not alter the melting point.

Department of Chemotherapy,
Kitasato Institute, Tokyo.

THE VISCOSITY OF VAPOURS OF ORGANIC COMPOUNDS. PART II.

By Toshizo TITANI.

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Experiments on the transpiration method have been continued for various organic gases, using the capillary viscosimeter recently devised by the writer.[1] As described in the preceding paper air has been taken as standard substance, its viscosity being assumed to be equal to Millikan's value 1823×10^{-7} at 23°C.; and the values for other substances have been determined by relative measurement. Present work includes the measurements for seventeen gases at temperatures ranging between 20° and 120°C. and the computation of Sutherland's constants and molecular diameters for each of them. The gases used and their preparations are as follows:

Ethane: obtained by the electrolysis of potassium acetate, thoroughly washed with potassium hydroxide solution, condensed and then repeatedly fractionated.

Propane and isobutane: obtained by the action of Zn–Cu couple on dilute alcoholic solution of isopropyl- or isobutyl-iodide, condensed and fractionated.

Normal butane: prepared by the action ef sodium amalgam on ethyl-iodide and purified by fractional distillation.

Ethylene and propylene: obtained by dehydrating ethyl- or iso-propyl-alcohol with hot concentrated phosphoric acid.

α- and β-butylene: obtained by the action of alcoholic potash on n-butyl- or secondary butyl-iodide and puried by fractional distillation.

γ-butylene: obtained by dehydrating tertiary butyl alcohol with hot anhydrous oxalic acid and purified by fractional distillation.

Isoamylene (isopropyl-ethylene): obtained by the action of alcoholic potash on isoamyl-iodide prepared from Kahlbaum's isoamyl alcohol, shaken with two volumes dilute sulphuric acid at 0°C. for two hours[2] and then fractionated.

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(1) This Bulletin, **4** (1929), 277.
(2) Wischnegradsky, *Ann.*, **190** (1878), 353.

Acetylene: prepared from calcium carbide and water and purified after Vanino.[1]

Allylene: obtained by the action of alcoholic potash on propylene-bromide, precipitated as copper compound, regenerated by warm dilute hydrochloric acid and fractionated.

Trimethylene: prepared by the reduction of trimethylene-bromide with zinc dust and alcohol, washed with potassium permanganate solution and fractionated.

Methyl-ether: obtained by dehydrating methyl alcohol with hot concentrated phosphoric acid, alcohol vapour mixed having been absorbed with phosphorus pentoxide.

Methyl-chloride: obtained by the action of dry hydrogen chloride gas on the boiling mixture of methyl alcohol and zinc chloride, washed with dilute potassium hydroxide solution and fractionated.

Methyl-bromide: obtained by heating the mixture of methyl alcohol, potassium bromide and dilute sulphuric acid, washed with water and fractionated.

Sulphur-dioxide: taken from a steel bomb and dried with sulphuric acid.

The gases hardly soluble in water were all thoroughly washed with water and dried with calcium chloride before distillation.

The results of measurements are shown in the following tables. Sutherland's formula has been found to be applicable with satisfactory results for all gases. The viscosity values calculated by this formula are given in the third column. For the sake of comparison other observers' values are also cited, of which the figures with asterisk have been estimated graphically from original observed values.

Ethane.

$$\eta = 107.15 \frac{T^{3/2}}{T+287.3} \cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$		Other observers' values
	Obs.	Calc.	
0	—	863	855 (Vogel[2] 1914)
20	929	926	917*(Ishida[3] 1923)
40	986	989	—
60	1050	1050	—
80	1111	1110	—
100	1167	1169	—
120	1230	1227	—

(1) Vanino, "Handbuch d. präparativen Chemie," II, 2. Aufl., (1923).
(2) Vogel, *Ann. Phys.*, **43** (1914), 1235.
(3) Ishida, *Phys. Rev.*, **21** (1923), 550.

Propane.

$$\eta = 102.3 \frac{T^{3/2}}{T+341.3} \cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$		Other observers' value
	Obs.	Calc.	
0	—	751	752 (Klemenc & Remi,(1) 1923)
20	806	809	—
40	873	866	—
60	922	922	—
80	978	977	—
100	1029	1032	—
120	1082	1085	—

Normal butane.

$$\eta = 98.27 \frac{T^{3/2}}{T+377.4} \cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$		Other observers' values
	Obs.	Calc.	
0	—	682	852*(Kuenen and Visser,(2) 1913)
20	739	735	—
40	787	789	—
60	839	841	—
80	885	893	—
100	947	944	1092 („)
120	998	994	—

Isobutane.

$$\eta = 92.85 \frac{T^{3/2}}{T+335.5} \cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$		Others observer's value
	Obs.	Calc.	
0	—	689	—
20	744	741	747*(Ishida(3) 1923)
40	792	793	—
60	845	844	—
80	888	895	—
100	947	944	—
120	995	993	—

(1) Klemenc and Remi, *Monatsh. Chem.*, **44** (1923), 307.

(2) Kuenen and Visser, *Verhandel. Akad. Wetenschappen Amsterdam*, **22** (1913), 336; *Comm. Phys. Lab. Univ. Leiden*, No. 138 a.

(3) Ishida, loc. cit.

Ethylene.

$$\eta = 107.0 \frac{T^{3/2}}{T + 259.1} \cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$		Other observers' values
	Obs.	Calc.	
0	—	907	966 (Graham,[1] 1846) 922 (v. Obermayer,[2] 1875) 961 (Breitenbach,[3] 1901) 907 (Zimmer,[4] 1911)
20	—	972	1090 (Graham) 987*(v. Obermayer) 1032*(Breitenbach) 974*(Zimmer)
22	970	979	—
40	1036	1036	—
60	1109 1106 } 1108	1098	1116*(v. Obermayer)
80	1155 1153 } 1154	1160	—
100	1223 1217 } 1220	1220	1280*(Breitenbach)
120	1278 1280 } 1279	1279	—

Propylene.

$$\eta = 103.2 \frac{T^{3/2}}{T + 321{\cdot}6} \cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$	
	Obs.	Calç.
0	—	783
20	835	842
21.5	856	847
40	893	901
60	959	958
80	1023	1015
100	1071	1070
120	1122	1125

(1) Graham, *Phil. Trans.*, **3** (1846), 573.
(2) v. Obermayer, *Wien. Ber.*, **71** [2a], (1875), 281.
(3) Breitenbach, *Ann. Phys.*, **5** (1901), 166.
(4) Zimmer, Diss. Halle, (1911); *Verhandl. deut. physik. Ges.*, **14** (1912), 471.

α—butylene.

$$\eta = 94.48 \frac{T^{3/2}}{T+328.9} \cdot 10^{-7}$$

t°C.	$\eta_l \cdot 10^7$	
	Obs.	Calc.
0	—	708
20	761	762
40	819	815
60	863	868
80	922	919
100	971	970
120	1020	1020

β—butylene.

$$\eta = 97.63 \frac{T^{3/2}}{T+362.1} \cdot 10^{-7}$$

t°C.	$\eta_l \cdot 10^7$	
	Obs.	Calc.
0	—	694
25	761	761
40	796	801
60	858	854
80	905	906
100	961	957
120	1005	1008

γ—butylene.

$$\eta = 99.21 \frac{T^{3/2}}{T+339.0} \cdot 10^{-7}$$

t°C.	$\eta_l \cdot 10^7$	
	Obs.	Calc.
0	—	732
30	815	815
40	843	843
60	897	897
80	949	951
100	1006	1004
120	1056	1056

Isoamylene (Isopropyl-ethylene).

$$\eta = 94.48 \frac{T^{3/2}}{T + 368.0} \cdot 10^{-7}$$

$t°$ C.	$\eta_t \cdot 10^7$	
	Obs.	Calc.
0	—	665
22	714	722
40	771	769
50	793	794
60	829	819
80	871	869
100	915	919
120	967	968

Acetylene.

$$\eta = 99.59 \frac{T^{3/2}}{T + 198.2} \cdot 10^{-7}$$

$t°$ C.	$\eta_t \cdot 10^7$		Other observer's value
	Obs.	Calc.	
0	—	954	943 (Vogel,[1] 1914)
20	1020	1017	—
40	1079	1079	—
50	1113	1110	—
60	1131	1140	—
80	1198	1199	—
100	1254	1256	—
120	1318	1313	—

Allylene.

$$\eta = 98.35 \frac{T^{3/2}}{T + 276.5} \cdot 10^{-7}$$

$t°$ C.	$\eta_t \cdot 10^7$	
	Obs.	Calc.
0	—	808
10	—	837
20	867	866
30	895	895
40	925	924
50	952	953
60	977	981
70	1009	1009
80	1039	1036
90	1066	1064
100	1090	1091

(1) Vogel, loc. cit.

Trimethylene.

$$\eta = 115.3 \frac{T^{3/2}}{T + 372.0} \cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$	
	Obs.	Calc.
0	—	807
20	876	870
40	923	933
50	960	964
60	999	994
80	1057	1055
100	1113	1115
120	1179	1175

Methyl-ether.

$$\eta = 116.4 \frac{T^{3/2}}{T + 344.9} \cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$		Other observers' values
	Obs.	Calc.	
0	—	850	905 (Graham,[1] 1846)
19.5	909	914	—
20	—	915	1020 (,,)
40	984	980	—
60	1044	1043	—
80	1109	1106	—
100	1167	1168	1190 (Pedersen,[2] 1907)
120	1228	1229	—

Methyl-chloride.

$$\eta = 142.3 \frac{T^{3/2}}{T + 380.1} \cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$		Other observers' values[3]
	Obs.	Calc.	
0	—	983	1025 (Graham, 1846) 989 (Breitenbach, 1901) 978 (Vogel, 1914)
10	—	1022	—
20	1061	1061	1160 (Graham) 1072*(Breitenbach)
30	1101	1099	—
40	1140	1137	—
50	1175	1175	—
60	1209	1213	—
70	1250	1251	—
80	1287	1288	—
90	1323	1325	—
100	1357	1362	1388*(Breitenbach)
110	1400	1398	—
120	1440	1434	—
130	1471	1470	—

(1) Graham, loc. cit. (2) Pedersen, *Phys. Rev.*, **25** (1907), 225. (3) Loc. cit.

Methyl-bromide.

$$\eta = 177.5 \frac{T^{3/2}}{T+379.2} \cdot 10^{-7}$$

$t°$ C.	$\eta \cdot 10^7$	
	Obs.	Calc.
0	—	1228
10	1277	1277
20	1327	1325
21	1333	1330
30	1378	1373
40	1420, 1412 } 1416	1421
50	1457	1468
60	1512, 1522 } 1517	1515
120	1797	1791

Sulphur-dioxide.

$$\eta = 173.6 \frac{T^{3/2}}{T+395.8} \cdot 10^{-7}$$

$t°$ C.	$\eta \cdot 10^7$		Other observers' values.
	Obs.	Calc.	
0	—	1171	1225 Graham,(1) 1846) 1183 (Vogel,(2) 1914) 1168 (Smith,(3) 1922)
20	1266	1265	1380 (Graham) 1263* (Smith) 1250* (Trautz and Weizel,(4) 1925)
40	1352	1357	1345* (,,)
60	1455	1448	—
80	1540	1538	1533* (Trautz and Weizel)
100	1622	1627	1630 (Smith) 1625* (Trautz and Weizel)
120	1716	1715	1720* (,,)

(1) Graham, loc. cit.
(2) Vogel, loc. cit.
(3) Smith, *Phil. Mag.*, [vi], **44** (1922), 508.
(4) Trautz and Weizel, *Ann. Phys.*, [4], **78** (1925), 305.

Sutherland's constants C for various gases are said to be proportional to the critical point T_K or the boiling point T_S expressed in absolute scale, being equal to $\frac{T_K}{1.12}$ according to Rankine[1] or to $1.47T_S$ according to Vogel.[2] The above results show that the relations do not hold strictly and the discrepancy from the rules is often remarkable, as is seen from the next table.

Sutherland's Constants.

Substance	$C_{obs.}$	$\frac{T_K}{1.12}$	$1.47\,T_S$	Other observers' values[3]
Ethane	287	275	272	—
Propane	341	330	335	323.7 (Klemenc and Remi)
Normal butane	377	380	400	349 (Kuenen and Visser)
Isobutane	336	363	387	—
Ethylene	259	253	249	272 (Sutherland) 226 (Breitenbach) 272 (O. E. Meyer and Zimmer)
Propylene	322	326	332	
α-butylene	329	372	393	
β-butylene	362	382	403	
γ-butylene	339	372	391	
Isoamylene	368	—	432	
Acetylene	198	276	278	
Allylene	277	360	366	
Trimethylene	372	—	350	
Methyl-ether	345	360	368	
Methyl-chloride	389	371	366	454 (Breitenbach)
Methyl-bromide	379	417	409	
Sulphur-dioxide	396	384	386	416 (Smith)
Air	113	118	119	Cf. the Part I of this paper

Mean free pathes (l) and collision diameters (σ) of molecules were calculated by the kinetic theory of gases using the following equations, where $\bar{u}$ expresses mean velocity, M molecular weight and n the number of molecules in one cubic centimeter, all referred to 0°C. and one atmospheric pressure.

(1) Rankine, *Proc. Roy. Soc. London*, [A], **84** (1910), 181.
(2) Vogel, loc. cit.
(3) Landolt-Börnstein-Roth, "Physikalisch-chemische Tabellen," I, 5. Aufl., (1923).

$$\bar{u}^2=\frac{8}{\pi}\frac{p}{d}=\frac{8}{\pi}\times 1\,013\,250\times\frac{22\,412}{M}$$

$$l=\frac{32\eta}{5\pi d\bar{u}}=\frac{\eta\times 22\,412}{0.49\times M\times\bar{u}}$$

$$\sigma^2=\frac{1}{\sqrt{2}\,n\pi l\left(1+\frac{C}{T}\right)}\cdot \qquad (n=2.7\times 10^{19})$$

The next table contains the results of calculation :

Substance	M	$\bar{u}$	$\eta\cdot 10^7$	$l\cdot 10^8$	C	$\sigma\cdot 10^8$
Ethane	30.05	43 870	863	299	287	3.68
Propane	44.06	36 230	751	215	341	4.15
Normal butane	58.08	31 550	682	170	377	4.53
Isobutane	58.08	31 550	689	172	336	4.66
Ethylene	28.03	45 420	907	326	259	3.62
Propylene	42.05	37 090	783	230	322	4.08
α-butylene	56.06	32 120	708	180	329	4.58
β-butylene	56.06	32 120	694	176	362	4.51
γ-butylene	56.06	32 120	732	186	339	4.47
Isoamylene	70.08	28 730	665	151	368	4.84
Acetylene	26.02	47 150	954	356	198	3.68
Allylene	40.03	38 010	808	243	277	4.13
Trimethylene	42.05	37 090	807	237	372	3.86
Methyl-ether	46.05	35 440	850	238	345	3.93
Methyl-chloride	50.48	33 850	983	263	380	3.64
Methyl-bromide	94.94	24 680	1 228	240	379	3.81
Sulphur-dioxide	64.06	30 040	1 171	278	396	3.49
Air	28.99	44 660	1 711	604	113	3.12

The molecular diameters (σ_η) thus calculated from viscosity agree generally with those (σ_b) from van der Waals' b, deduced from critical data[1] as is seen in the following table.

(1) Valentiner, Landolt-Börnstein-Roth, "Physikalisch-chemische Tabellen," I, 5. Aufl., (1923), 253; Pickerring, *J. Phys. Chem.*, **28** (1924), 97.

Molecular diameters.

Substance	$\sigma_\eta \cdot 10^8$	$\sigma_b \cdot 10^8$	$\sqrt[3]{V_S}$
Ethane	3.68	3.70	3.84
Propane	4.15	4.05	4.21
Normal butane	4.53	4.59	4.58
Isobutane	4.66	4.48	4.57
Ethylene	3.62	3.56	3.54
Propylene	4.08	4.02	4.05
α-butylene	4.58	—	4.46
β-butylene	4.51	—	4.46
γ-butylene	4.47	—	4.45
Isoamylene	4.84	4.80	4.79
Acetylene	3.68	3.44	3.33
Allylene	4.13	—	3.90
Trimethylene	3.86	—	3.92
Methyl-ether	3.93	3.85	3.97
Methyl-chloride	3.64	3.71	3.69
Methyl-bromide	3.81	—	3.82
Sulphur-dioxide	3.49	3.55	3.53
Air	3.12	3.06	3.11

The figures in the last column express the cube root of the molecular volumes at boiling points. These values shall be proportional to the actual diameters of molecules according to the theory of corresponding state and it seems to be actually the case. Indeed, if 10^{-8} be affixed to the figures in the last column, they express the actual dimensions of molecules. This result shows the molecular volumes at boiling points being about three times as large as the actual volume of molecules:

$$6.06 \times 10^{23} \cdot \frac{\pi}{6} \sigma^3 \fallingdotseq 0.318 V_s .$$

In conclusion the writer wishes to express his cordial thanks to Prof. M. Katayama for this kind guidance and encouragement throughout this experiment.

The Institute of Physical and Chemical Research.
Hongo, Tokyo.

A SERIES OF CONDENSATIONS PRODUCING THE ESTERS OF ACETYL-PROPYLENE-CARBOXYLIC ACIDS.

By Yoshiyuki URUSHIBARA.

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In the previous paper on "peculiarity in the formation of the nitrile-esters of dicarboxyglutaconic acid"[1] the author pointed out the fact that in the condensation of the ethoxymethylene-compound $XYC=CHOC_2H_5$ with the sodio-methylene-compound $CHNaX'Y'$, if it is carried out in the ethereal medium, the following four products are possible:
$XYC=CH-CNaX'Y'$; $X'Y'C=CH-CNaXY$; $X'Y'C=CH-CNaX'Y'$; $XYC=CH-CNaXY$.

That paper mainly dealt with the cases where each of X, X', Y, and Y' was either CN or $COOC_2H_5$. In the present paper the results of the condensations where the acetyl-group acts in place of the nitrile-group will be reported.

As a whole, similar results have been obtained, which are shown in the table. The found products are placed in the forms of the sodium derivatives under the general formulae showing the kinds, the blank spaces corresponding to those which could not be found inspite of their formation being possible.

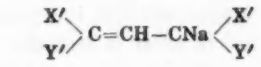
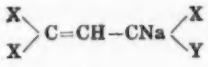
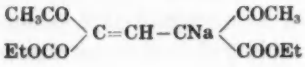
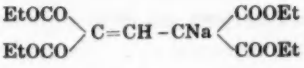
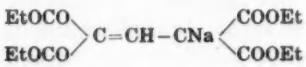
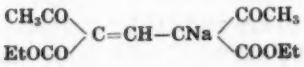
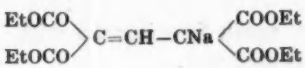
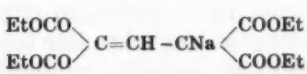
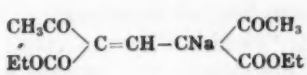
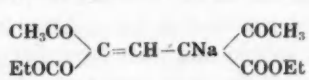
But, unfortunately, the products of the first and the second kinds must be considered under the following unfavourable conditions: There have been no method to determine the positions of the sodium atom and the double union; there was no condensation in which both the first and second products were found; and moreover, as shown in the experimental part, it was impossible to determine whether the products of a pair of condensations were identical or not, except condensations 1 and 2. These conditions make the results somewhat indefinite, for it is impossible to determine whether a product belongs to the first kind or the second. In the table such compounds are placed in partly expanded formulae. Nevertheless, the author believes that four products are also theoretically possible in each of these condensations.

Experimental Part.

Experimental Procedure in General. The methylene compound is converted into the sodium derivative by adding it to finely granulated metallic sodium covered with pure ether. To the sodio-methylene compound in ether a

(1) This Bulletin, 5 (1930), 1.

	Condensations.	Products	
		The first kind	The second kind
	$\begin{matrix}X\\Y\end{matrix}\!\!>\!C{=}CHOEt+CHNa\!<\!\!\begin{matrix}X'\\Y'\end{matrix}$	$\begin{matrix}X\\Y\end{matrix}\!\!>\!C{=}CH{-}CNa\!<\!\!\begin{matrix}X'\\Y'\end{matrix}$	$\begin{matrix}X'\\Y'\end{matrix}\!\!>\!C{=}CH{-}CNa\!<\!\!\begin{matrix}X\\Y\end{matrix}$
1	$\begin{matrix}CH_3CO\\EtOCO\end{matrix}\!\!>\!C{=}CHOEt+CHNa\!<\!\!\begin{matrix}COCH_3\\COOMe\end{matrix}$	$\begin{matrix}CH_3CO\\EtOCO\end{matrix}\!\!>\!C{=}CH{-}CNa\!<\!\!\begin{matrix}COCH_3\\COOMe\end{matrix}$	
2	$\begin{matrix}CH_3CO\\MeOCO\end{matrix}\!\!>\!C{=}CHOEt+CHNa\!<\!\!\begin{matrix}COCH_3\\COOEt\end{matrix}$	$\begin{matrix}CH_3CO\\MeOCO\end{matrix}\!\!>\!C{=}CH{-}CNa\!<\!\!\begin{matrix}COCH_3\\COOEt\end{matrix}$	
3	$\begin{matrix}EtOCO\\EtOCO\end{matrix}\!\!>\!C{=}CHOEt+CHNa\!<\!\!\begin{matrix}COCH_3\\COOEt\end{matrix}$	$\begin{matrix}EtOCO\\EtOCO\end{matrix}\!\!>\!(C_3HNa)\!<\!\!\begin{matrix}COCH_3\\COOEt\end{matrix}$	
4	$\begin{matrix}CH_3CO\\EtOCO\end{matrix}\!\!>\!C{=}CHOEt+CHNa\!<\!\!\begin{matrix}COOEt\\COOEt\end{matrix}$	$\begin{matrix}CH_3CO\\EtOCO\end{matrix}\!\!>\!(C_3HNa)\!<\!\!\begin{matrix}COOEt\\COOEt\end{matrix}$	
5	$\begin{matrix}EtOCO\\EtOCO\end{matrix}\!\!>\!C{=}CHOEt+CHNa\!<\!\!\begin{matrix}COCH_3\\COCH_3\end{matrix}$	$\begin{matrix}EtOCO\\EtOCO\end{matrix}\!\!>\!(C_3HNa)\!<\!\!\begin{matrix}COCH_3\\COCH_3\end{matrix}$	
6	$\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!\!>\!C{=}CHOEt+CHNa\!<\!\!\begin{matrix}COOEt\\COOEt\end{matrix}$	$\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!\!>\!(C_3HNa)\!<\!\!\begin{matrix}COOEt\\COOEt\end{matrix}$	
7	$\begin{matrix}CH_3CO\\EtOCO\end{matrix}\!\!>\!C{=}CHOEt+CHNa\!<\!\!\begin{matrix}COCH_3\\COCH_3\end{matrix}$		
8	$\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!\!>\!C{=}CHOEt+CHNa\!<\!\!\begin{matrix}COCH_3\\COOEt\end{matrix}$		

The third kind	The fourth kind
	
	
	
	
	
	
	

calculated amount of the ethoxymethylene compound diluted with pure ether is added gradually under constant stirring. The mixture is kept at the room temperature for a length of time, during which the colour of the mass grows from yellow to red, and, after relatively long standing, to dark red. Then water is added to the mass. If the sodium derivative of tetraethyl dicarboxyglutaconate is present in a large quantity, it crystallises from the aqueous solution after a short time. If such is the case, the crystals are collected, and treated separately. The aqueous solution is acidified with dilute hydrochloric or sulphuric acid, and the separating substance is extracted with ether. If any solid substance difficulty soluble in ether be present, it is filtered. The ethereal solution is shaken many times with small volumes of a ten percent aqueous solution of sodium carbonate, and in this way the substance in ether is fractionated into several parts in the grade of acidity. Most of the red colouring matter is taken in the first few fractions. If tetraethyl dicarboxyglutaconate be present, its sodium derivative separates out in yellow crystals towards the end of the fractional extraction with sodium carbonate, and then this is collected. These fractions are separately acidified with hydrochloric acid, when oil or crystals separate out. Here, if it can be considered that some numbers of successive fractions are of the same nature, they are united together, and afterall the whole is divided into five or six fractions. Crystalline substances are purified by recrystallisation from carbon bisulphide and ligroin; oils are extracted with ether and the ethereal solutions are washed with water, dried, and evaporated in vacuum. These purified substances are subjected to analysis and identification. If necessary, oils are dissolved in ether, again fractionated with soda solutions, and the seemingly purest part is analysed.

The red substance in the condensation mass, the crystalline substance separating on acidifying the aqueous solution of the condensation mass and difficulty soluble in ether, and the red colouring matter taken into the soda extracts, are all of the similar nature. These are probably xanthophanic acids[1] or similar compounds; but as they are not the objects of the present investigation, no experiment on these substances was carried out.

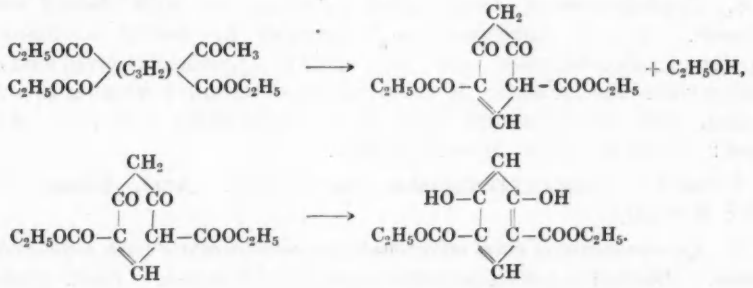
1. *Condensation of ethyl ethoxymethylene-acetoacetate with methyl sodio-acetoacetate.*[2] α-Methyl γ-ethyl α,γ-diacetylglutaconate was isolated. The substance, obtained by recrystallising the crude product three times from carbon bisulphide and once from ligroin, melted at 74°. After it was recrystallised twice more from carbon bisulphide and once from ligroin, it melted at 76°, but the melting point was, none the less, unsharp. Accord-

(1) Claisen, *Ann.*, **297** (1897), 48.
(2) Cf. Feist, *Ber.*, **59** (1926), 2958.

ing to Feist this compound melts at 73°, and, as he states, it seems difficult to purify it.

2. *Condensation of methyl ethoxymethylene-acetoacetate with ethyl sodio-acetoacetate.*[1] γ-Methyl α-ethyl α,γ-diacetylglutaconate was isolated. The substance, recrystallised three times from carbon bisulphide and once from ligroin, melted at 85°, and after it was recrystallised further twice from carbon bisulphide and once from ligroin, it melted sharply at 90°. According to Feist the melting point of this substance is 87°.

3. *Condensation of diethyl ethoxymethylene-malonate with ethyl sodio-acetoacetate.* An oily fraction, on standing, changed into a crystalline mass. This was recrystallised from carbon bisulphide. Anal. Found: C=56.83; H=5.53%. Calc. for $C_6H_7O_3$: C=56.67; H=5.55%. Melting point: 77°. Molecular weight: about 220. If $C_{12}H_{14}O_6$ be the molecular formula of the substance, it is less C_2H_6O or C_2H_5OH than a triethyl acetyl-carboxy-glutaconate $C_{14}H_{20}O_7$, one of the expected products of this condensation. It is, therefore, most natural to suppose the formation of a triethyl acetyl-carboxy-glutaconate, the product of the first or the second kind, and to consider the substance $C_{12}H_{14}O_6$ a derivative of resorcine produced by the following reactions:



Besides the above substance, diethyl α, γ-diacetyl-glutaconate was isolated. Anal. Found: C=57.67, 57.59; H=6.69, 6.70%. Calc. for $C_{13}H_{18}O_6$: C=57.78; H=6.67%. Melting point: 93°. The melting point observed by Claisen is 96°.

Further tetraethyl α,γ-dicarboxyglutaconate was isolated. Anal. Found: C=54.68; H=6.74%. Calc. for $C_{15}H_{22}O_8$: C=54.51; H=6.72%.

4. *Condensation of ethyl ethoxymethylene-acetoacetate with diethyl sodio-malonate.* From the fraction which was expected to be consisted of diethyl diacetylglutaconate an oil giving the following analytical results

(1) Cf. Feist, loc. cit.

was obtained. Anal. Found: C=57.57; H=6.39%. This seems to have been impure diethyl diacetyl-glutaconate.

The same resorcine derivative as obtained in condensation 3 was isolated. Anal. Found: C=56.75; H=5.63%. This indicates the formation of a triethyl acetyl-carboxy-glutaconate; but, as the isolated substance $C_{12}H_{14}O_6$ is not the direct product, it is impossible to determine whether this triethyl acetyl-carboxy-glutaconate is the first kind or the second, and whether it is identical with the triethyl acetyl-carboxy-glutaconate of condensation 3.

Further tetraethyl dicarboxyglutaconate was isolated. Anal. Found: C=54.42; H=6.73%.

5. *Condensation of diethyl ethoxymethylene-malonate with sodio-acetyl-acetone.* An oily compound giving an analytical result corresponding to diethyl α,α-diacetyl-propylene-γ,γ-dicarboxylate or to diethyl γ,γ-diacetyl-propylene-α,α-dicarboxylate was isolated. Anal. Found: C=57.61, 57.13; H=6.63, 6.66%. Calc. for $C_{13}H_{18}O_6$: C=57.78; H=6.67%.

Tetraethyl dicarboxyglutaconate was isolated. Anal. Found: C=54.76; H=6.76%.

6. *Condensation of ethoxymethylene-acetylacetone with diethyl sodio-malonate.* An oil corresponding in analysis to diethyl α,α-diacetyl-propylene-γ,γ-dicarboxylate or to diethyl γ,γ-diacetyl-propylene-α,α-dicarboxylate was isolated. It could not be determined whether this was identical with the substance obtained in condensation 5 or not. Anal. Found: C=57.61, 57.43; H=6.66, 6.66%.

Tetraethyl dicarboxyglutaconate was isolated. Anal. Found: C=54.22; H=6.66%.

7. *Condensation of ethyl ethoxymethylene-acetoacetate with sodio-acetyl-acetone.* Diethyl α,γ-diacetylglutaconate was isolated. Anal. Found: C=57.80; H=6.66%.

8. *Condensation of ethoxymethylene-acetylacetone with ethyl sodio-acetoacetate.* Diethyl α,γ-diacetylglutaconate was isolated. Anal. Found: C=57.76; H=6.55%. Melting point: about 92°.

The same condensation as condensation 4, that is the condensation of ethyl ethoxymethylene-acetoacetate with diethyl sodio-malonate, was carried out in alcohol. Diethyl α, γ-diacetylglutaconate (C=57.80; H=6.63%), the product of the fourth kind, and tetraethyl α, γ-dicarboxyglutaconate (C=54.37; H=6.69%), the product of the third kind, were isolated. This experiment shows that there is no fundamental difference between the condensations in alcohol and those in ether.

The author expresses his hearty thanks to Prof. K. Matsubara for his kind inspection of this paper.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.